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DEPARTMENT 190-2

# SURFACE TREATMENT OF METALS, METHOD OF TESTING WITH RADIO-ACTIVE ISOTOPES

FINAL REPORT

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CONVAIR
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# SURFACE TREATMENT OF METALS, METHOD OF TESTING WITH RADIOACTIVE ISOTOPES

## ABSTRACT

An experimental technique is described for nondestructive testing of bond strength for aluminum metal surfaces bonded with organic adhesives.

The need for this development was prompted by previous work, by the author, which proved that the widely used water-drop method described by Franklin Institute Research Laboratories was unreliable.

The new technique uses radioactive tracers ($C^{14}$) in stearic acid to determine the amount of soil removed during cleaning operation. It also uses chromate ion ( $Cr^{51}$ ) in FPL solution, (sodium dichromate sulfuric acid), during the deoxidizing and etch treatment. The correlation between $Cr^{+6}$ sorbtion and bond strength was demonstrated as approximately linear.

## SURFACE TREATMENT OF METALS, METHOD OF TESTING WITH RADIOACTIVE ISOTOPES

### SUMMARY

The relationship of adhesive bond strength with the cleanliness and surface preparation of clad aluminum 2024-T3 was established.

This investigation was carried out in two phases. First the degree to which each of a group of metal cleaners removed soil from an aluminum surface was quantitatively determined by applying a "soil" material, stearic acid, tagged with radioactive carbon-14, and chromium-51. Secondly, the performance of FPL cleaner, sodium dichromate acid solution was more intensively investigated than that of other cleaners.

It appears from these studies that no direct correlation exists between degree of cleanliness per se and bond strength. However, FPL treated surfaces exhibited a marked correlation to bond strength if sufficient number of chromium hexavalent ions were adsorbed on the aluminum surface.

It was also evident that the reason FPL solution deteriorates with usage was due to accumulation of certain residual ions such as $Cr^{+3}$, Cl, Al and others. However, quantitative measurements were not conducted.

Finally, shop application of these findings by the Quality Control Department was recommended.

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I. PROJECT TITLE

Surface Treatment of Metals, Method of Testing With Radioactive Isotopes (Continuation of PR #896).

II. STATEMENT OF PROBLEM

Present methods of testing the efficiency of cleaning processes are unreliable. The proposed method uses radioactive isotopes and is considerably more reliable than any other method known to industry. Tests are required to corroborate initial findings.

III. OBJECTIVE AND PURPOSE

Correlation of surface ion adsorbtion of chromates on metal surfaces to bonding strength, using polymers as the bonding medium.

Purpose:

The purpose is to develop a technique of evaluating, by means of isotopes, the efficiency of surface-cleaning solutions.

IV. CONCLUSIONS

It appears from these studies that no direct correlation exists between degree of cleanliness or soil removal by aluminum cleaners and subsequent bond strengths on the aluminum surfaces cleaned. FPL-treated surfaces show excellent bonding strength even when these surfaces are not completely cleaned. However, this cannot be interpreted to mean that a clean surface is not important to a good bond.

Aluminum surfaces adsorb chromium ions from dichromate solutions to an extent proportional to the concentration of the chromate ion in the solution in the range considered.

IV. CONCLUSIONS (continued)

Adhesive tensile shear and peel tests indicate that there is a regular increase in bond strength corresponding to increased chromium deposition on the surface of the aluminum.

The strength of an adhesive bond is influenced by a number of variables. Cleanliness and chromium adsorption discussed here, may not be entirely responsible for surface conditions which permit a strong adhesive bond on aluminum. Nevertheless, it is possible that a variable, such as chromium adsorption may reflect the action of other variables and in this way may be used as an index of good surface preparation.

V. RECOMMENDATIONS

This project should be continued in three separate areas:

1. Develop application procedure for the use of isotopes in FPL shop cleaning solution for routine quality control tests.

2. Determine the effect of presence of aluminum, sulfate, chloride, zinc, copper, chromic (+3 ) ions to adsorption potential of chromate (+ 6) ion on metal surfaces in correlation to bond strength.

3. Determine the mechanism of bond failure by means of tagged adhesive primer, tagged tape, and tagged metal.

VI DEVELOPMENT OF THE PROJECT

Introduction:

Destructive tests of adhesive bonds on aluminum during 1957 cost Convair close to one million dollars. In an effort to reduce this cost Convair began a study of adhesive bonding on aluminum which has as its objective the dev-

## VI. DEVELOPMENT OF THE PROJECT

**Introduction:** (continued)

elopment of a non-destructive test for bond strength, or a method of predicting bond strength from some measurable property of the aluminum surface.

Previous investigations of cleaning treatments for aluminum alloys prior to adhesive bonding showed that Forest Products Laboratories cleaner (FPL), a sulfuric-acid sodium-dichromate solution, was superior to other known cleaning treatments. Specimens cleaned in FPL solution show a clean, etched surface which supports a strong adhesive bond. As the sulfuric acid and dichromate concentrations drop during use of the solution, bond strength also drops. ( See Figure 1 )

When the solution is recharged with sulfuric acid and dichromate, the aluminum processed again bonds well. After a number of additions of acid and dichromate, the solution fails to regain its ability to produce good aluminum surfaces, presumably because it has become contaminated with heavy concentrations of aluminum salts and reduced chromium salts. If more acid and dichromate are added to the solution at the end of the cycle indicated in the graph as terminal, the solution crystallizes.

Two explanations for this superiority of FPL in producing surfaces on aluminum which are conducive to the formation of strong adhesive bonds were considered and investigated:

1. FPL does a superior cleaning job. ( On the supposition that strength of adhesive bonds is directly correlated with cleaniness )

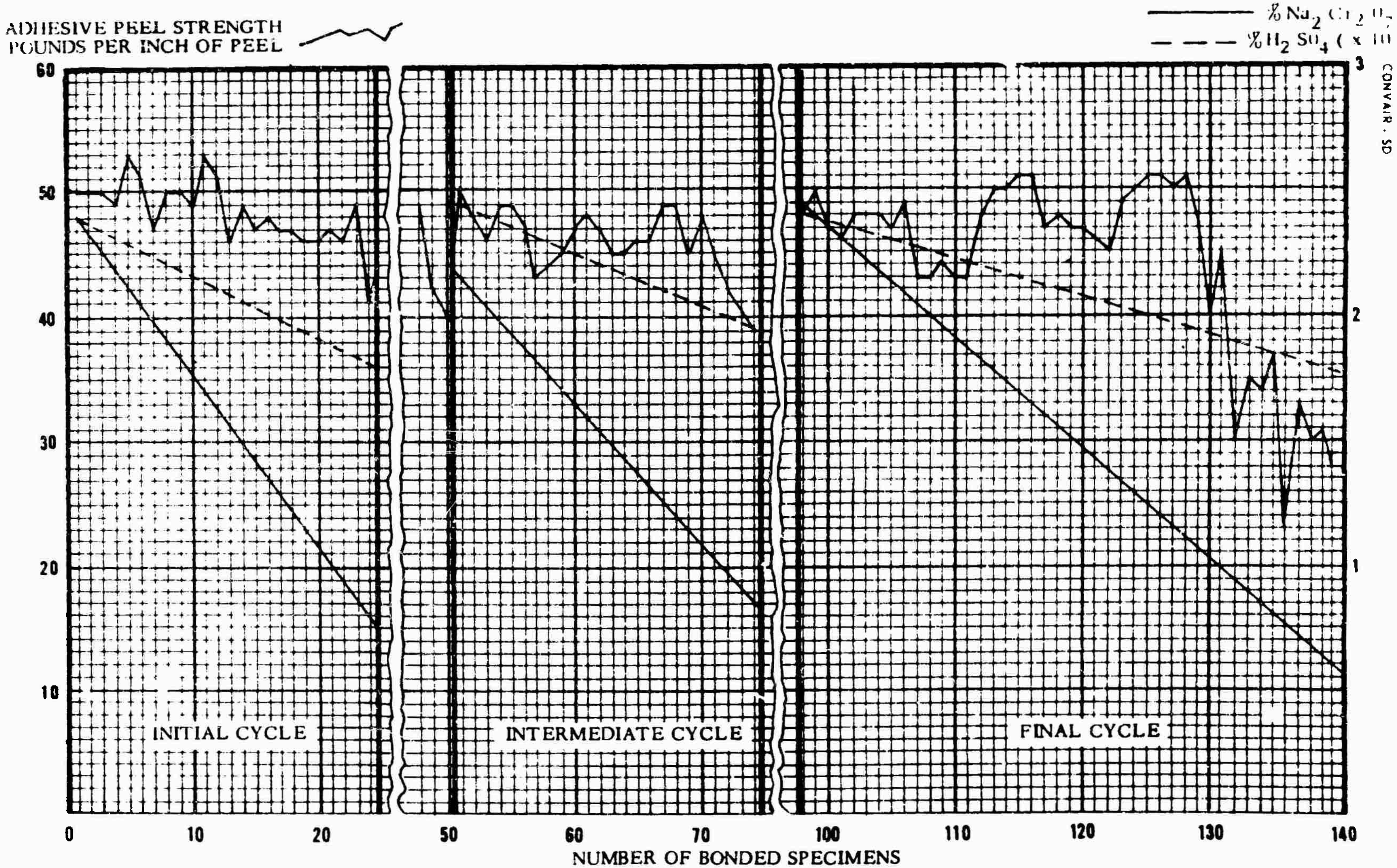


FIGURE 1 - EFFECTS OF SOLUTION DEPLETION ON $Na_2Cr_2O_7$ AND $H_2SO_4$ WITH CORRESPONDING BOND STRENGTHS. BARE 2024 - T86 ALUMINUM ALLOY METLBOND 4021 ADHESIVE ROOM TEMPERATURE TESTS

## VI. DEVELOPMENT OF THE PROJECT

Introduction: (continued)

2. FPL produces modifications on the aluminum surfaces which favor strong adhesive bonds.

The use of radioisotopes implemented both investigations. In the first study, that of cleaning efficiency, aluminum surfaces were uniformly contaminated with stearic acid which had been tagged with radioactive carbon-14. The degree to which it was removed by cleaners could then be determined. In the second study, sodium dichromate solutions were tagged with radioactive chromium-51 so that the concentration of chromium on the aluminum surfaces could be followed.

### Experimental: Procedure and Results:

A. Correlation of Adhesive Bond Strength with the Cleanliness of the Bonded Surface:

This investigation was carried out in two phases. First, the degree to which each of a group of metal cleaners removed soil from an aluminum surface was quantitatively determined by applying a soil material, tagged with radioactive carbon-14. The amount of soil present on the surface before and after cleaning was calculated from the amount of radioactivity present on the surface in each case.

The test specimens used to test the cleaning efficiency of the various cleaning treatments were made from stock 0.063-inch 2024-T3 clad aluminum alloy. Circular discs, 1.75-inch in diameter, were punched from a single sheet of this material. The protective paper was removed from the discs

VI. DEVELOPMENT OF THE PROJECT

Experimental: Procedure and Results: (continued)

and the metal surface cleaned as follows:

a) Hand wiped with methyl ethyl ketone

b) Washed with a sodium lauryl sulfate solution

c) Rinsed with acetone and allowed to dry

The cleaned discs were then contaminated with stearic acid which was tagged with carbon-14. Stearic acid was chosen as the soil because it is typical of the fatty acids which are present in polishing materials and are likely to be present on metal surfaces. The stearic acid was dissolved in kerosene and applied to the surface of the aluminum discs by means of a mechanical spreading device which distributed the soil uniformly. The discs were dried and a count of the radioactivity present on the surface of each was made using an NRD gasflow proportional counter together with a scaler.

The discs were than cleaned with various metal cleaners at recommended temperatures and times of immersion. Following this, another count was made of the radioactivity present on the surface and the amount of soil removed expressed as the ratio of the difference between the two counts and the count before cleaning. (See Table I )

Modified FPL solution ( 4 parts $Na_2Cr_2O_7$ 2H 0, 10 parts $H_2SO_4$, 30 parts $H_2O$ by weight ) was the most efficient cleaner tested. The commercial alkaline cleaner and the commercial acid cleaner followed in rank order. In varying temperature and times of immerison, the commercial acid cleaner behaved

TABLE I

RELATIVE CLEANING EFFICIENCIES OF VARIOUS METAL CLEANERS

AT THEIR RECOMMENDED TEMPERATURES AND TIMES OF IMMERSION

| CLEANER | SOLUTION TEMPERATURE | TIME OF IMMERSION | AVERAGE PERCENT SOIL REMOVED |
|---|---|---|---|
| FPL Solution | 150° F | 10 Minute | 98.2 |
| Commercial Alkaline Cleaner | 100° F | 5 Minute | 91.5 |
| Vapor Degrease | - | 2 Minut | 62.2 |
| MEK Hand Wipe | - | - | 58.0 |
| Commercial Acid Cleaner | Room Temperature | 20 Minute | 46.4 |

VI. DEVELOPMENT OF THE PROJECT

Experimental: Procedure and Results: (continued)

erratically and at no time removed more than 62% of the contamination present. The commercial alkaline cleaner performed almost as well at room temperature as at 100° F, indicating a possible chemical reaction between the stearic acid and alkaline components of the solution.

The performance of FPL cleaner was more intensively investigated than that of the other cleaners. The effect of time and temperature variables and the effect of aging or depletion of hexavalent chromium concentration on its cleaning efficiency were determined using the radioactive soil removal technique. (See Figure 2, 3, & 4)

FPL cleaner apparently may be used within a rather wide range of temperatures and immersion times. It is probable that 150° ± 5° F is the optimum temperature for cleaning with ten minute immersion time.

In the second phase of this investigation, tests of the adhesive bond strength on aluminum surfaces cleaned with the various cleaners considered in the first phase were made to determine whether or not there exists a direct correlation between bond strength and the cleanliness of the surface which is bonded. Specimens were made up for both peel tests and tensile shear tests were run at both room temperature and -67° F. [1] (next page)

All adhesive test specimens were contaminated with a solution of stearic acid (5% in kerosene) to duplicate the soil concentration as studied in the radiochemical phase. Specimens were then cleaned using the same

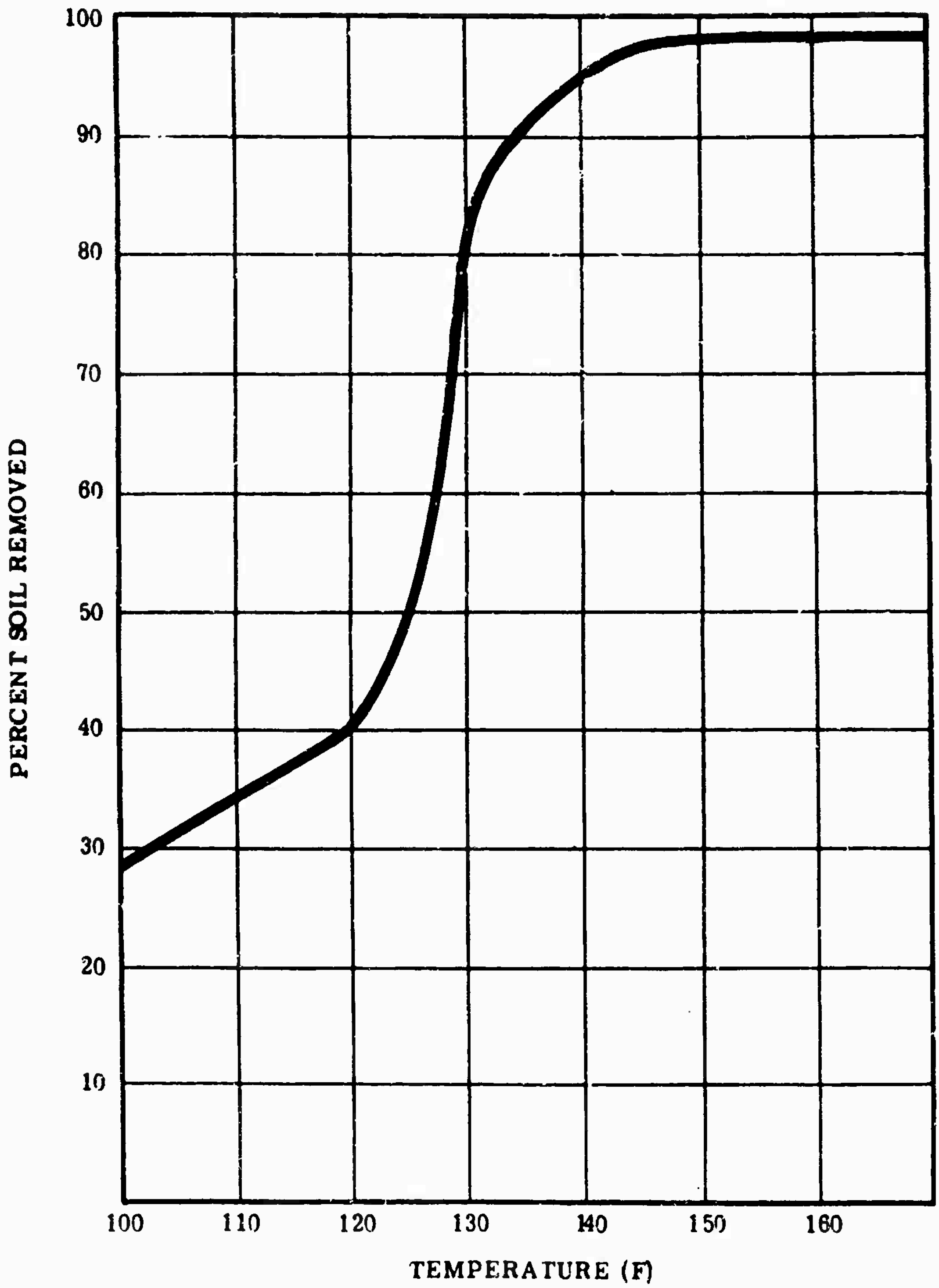


FIGURE 2 - F. P. L. SOLUTION - TIME OF IMMERSION = 10 MINUTES

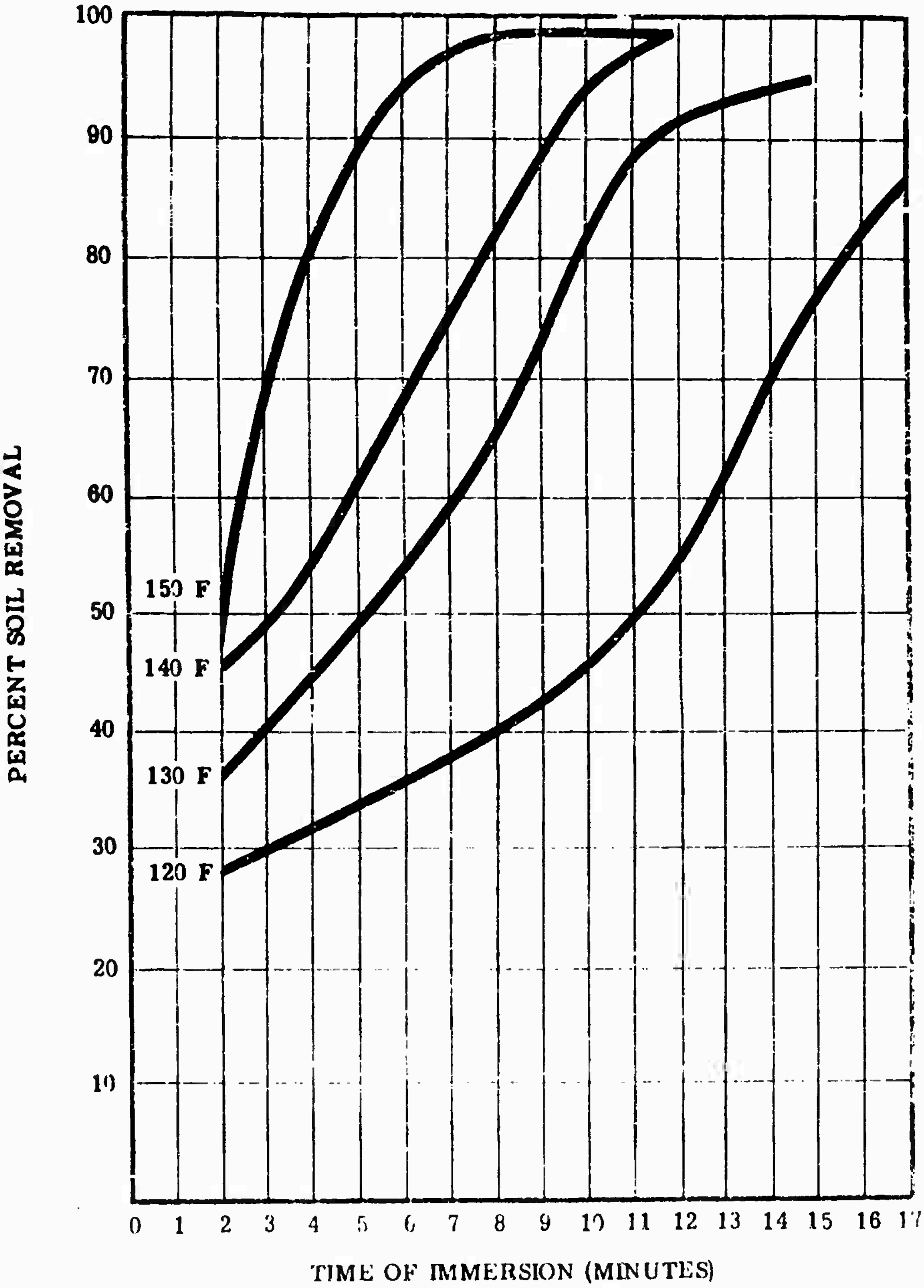


FIGURE 3 - F. P. L. SOLUTION (VARIABLE TIME AND TEMPERATURE)

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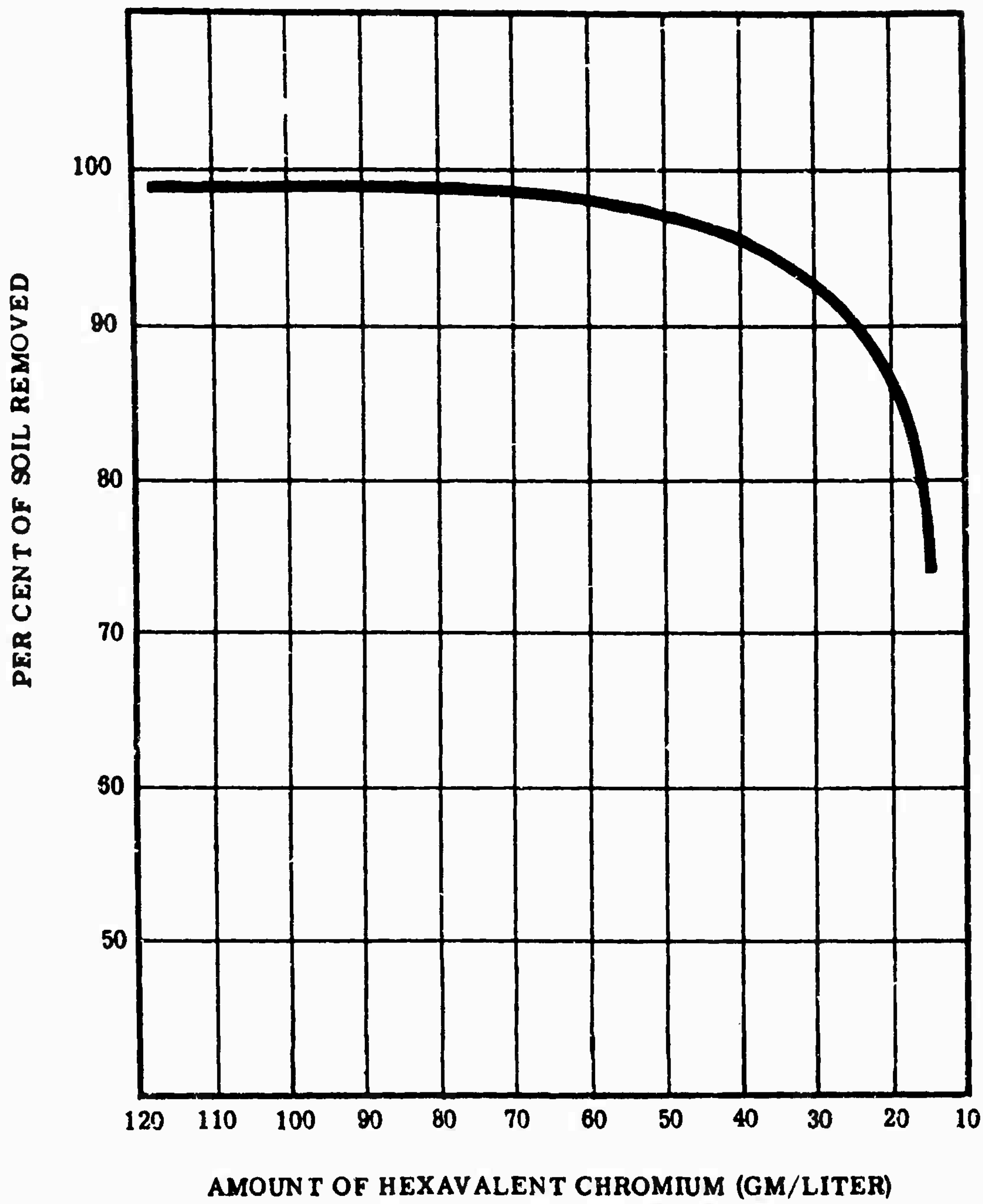


FIGURE 4 - AGED F. P. L. SOLUTION
TIME OF IMMERSION = 10 MINUTES
TEMPERATURE = 150 F
ORIGINAL $Cr^{+6}$ CONCENTRATION = 118 GM/LITER

VI. DEVELOPMENT OF THE PROJECT

Experimental: Procedure and Results: (continued)

cleaners which were used to clean the radioactive "soil" from the discs, earlier. Following this, the specimens were tested for adhesive strength.

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1. Standard metal-to-metal, adhesive peel specimens were used for most tests. A sheet of 0.020-inch 2024-T3 clad aluminum alloy was selected from stock to make the peel specimens. Specimens measuring 1 x 9 inches were sheared from sheet, processed and bonded together to produce peel specimens. Specimens were hand wiped with methyl ethyl ketone, cleaned by various procedures, and sprayed with a thin prime coat of Metlbond 4021, Type-II. The prime was allowed to dry 15 minutes at ambient temperature, and was subsequently baked at 250° F for 30 minutes. A single layer of Metlbond 4021, Type I was sandwiched between two of the prepared specimens, and cured in an electrically heated, hydraulic platen press for one hour at 350° F with 100 psi bonding pressure. Peel specimens were tested in the Convair drum-type honeycomb peel tester, adapted for metal-to-metal peel specimens. The peeling rate was 11 inches per minute. The Metlbond products are manufactured by Narmco Industries, Inc.

Tensile shear specimens were cut from 0.064-inch 2024-T3 clad aluminum alloy to make "finger panels". Specimens were bonded with 1/2-inch overlap. Processing was the same as for peel specimens. Tensile shear specimens were tested in a Tinius Olsen Hydraulic Testing Machine. Cooling to -67° F was accomplished using isopropyl alchol and dry ice. ( See Tables II and III )

## TABLE II

**PEEL STRENGTH OF METLBOND 4021 ADHESIVE ON 2024-T3 CLAD ALUMINUM ALLOY CLEANED BY VARIOUS METHODS**

(VALUES ARE AN AVERAGE OF 5 SPECIMENS)

| CLEANING PROCEDURE | PEEL STRENGTH (LBS/INCH PEEL) |
|---|---|
| Hand Wipe with Dry Cheesecloth | 4 |
| Hand Wipe with MEK | 5 |
| Rinse in Hot $H_2O$ (130° F) | 5 |
| Vapor Degrease | 5 |
| Commercial Alkaline Cleaner | 12 |
| Commercial Acid Cleaner | 22 |
| FPL Solution | 51 |

TABLE III

**TENSILE SHEAR STRENGTH OF METLBOND 4021 ADHESIVE ON 2024-T3 CLAD ALUMINUM ALLOY CLEANED BY VARIOUS METHODS**

(VALUES ARE AN AVERAGE OF 8 SPECIMENS)

| CLEANING PROCEDURE | TENSILE SHEAR STRENGTH - (PSI) | |
|---|---|---|
| | ROOM TEMP. | -67° F |
| Hand Wipe with Dry Cheesecloth | 2760 | 2880 |
| Hand Wipe with MEK | 2890 | 3240 |
| Rinse in Hot $H_2O$ ( 130° F) | 2810 | 2920 |
| Vapor Degrease | 2370 | 2180 |
| Commercial Alkaline Cleaner | 3430 | 3440 |
| Commercial Acid Cleaner | 3410 | 3160 |
| FPL Solution | 4840 | 4920 |

VI. DEVELOPMENT OF THE PROJECT

Experimental: Procedure and Results: (continued)

As in the cleaning tests, FPL was more intensively investigated from the aspect of the effect of time and temperature variables in the cleaning process and their effect on bond strength. This information was then combined with the data from the radiochemical phase to illustrate the relationship between the degree of cleanliness of an aluminum surface and bond strength. (See Figure 5 & 6 )

B. Correlation of Adhesive Bond Strength with Surface Ion Adsorption:

This comprises the second phase of this project.

Following the cleaning efficiency tests, a program was initiated to determine a possible correlation between chromium adsorption from sodium dichromate solutions on aluminum surfaces and subsequent adhesive bond strength.

Chromium adsorption isotherms were determined by subjecting 1.75-inch diameter aluminum discs ( Al. Alloy 2024-T3 clad, gauge 0.063-inch ) to solutions of sodium dichromate in concentrations of $10^{-1}$, $10^{-2}$, and $10^{-3}$ molar and containing radioactive chromium-51 as a tracer in the form of chromate ion. The ratios of non-active to radioactive chromium in the solutions were approximately $1 \times 10^{7}$, $6 \times 10^{6}$, and $1 \times 10^{6}$, respectively.

In an effort to make the surfaces as uniform as possible, the discs were immersed in boiling concentrated nitric acid for two minutes, removed , and rinsed thoroughly in distilled water prior to placing them in the dichromate solutions.

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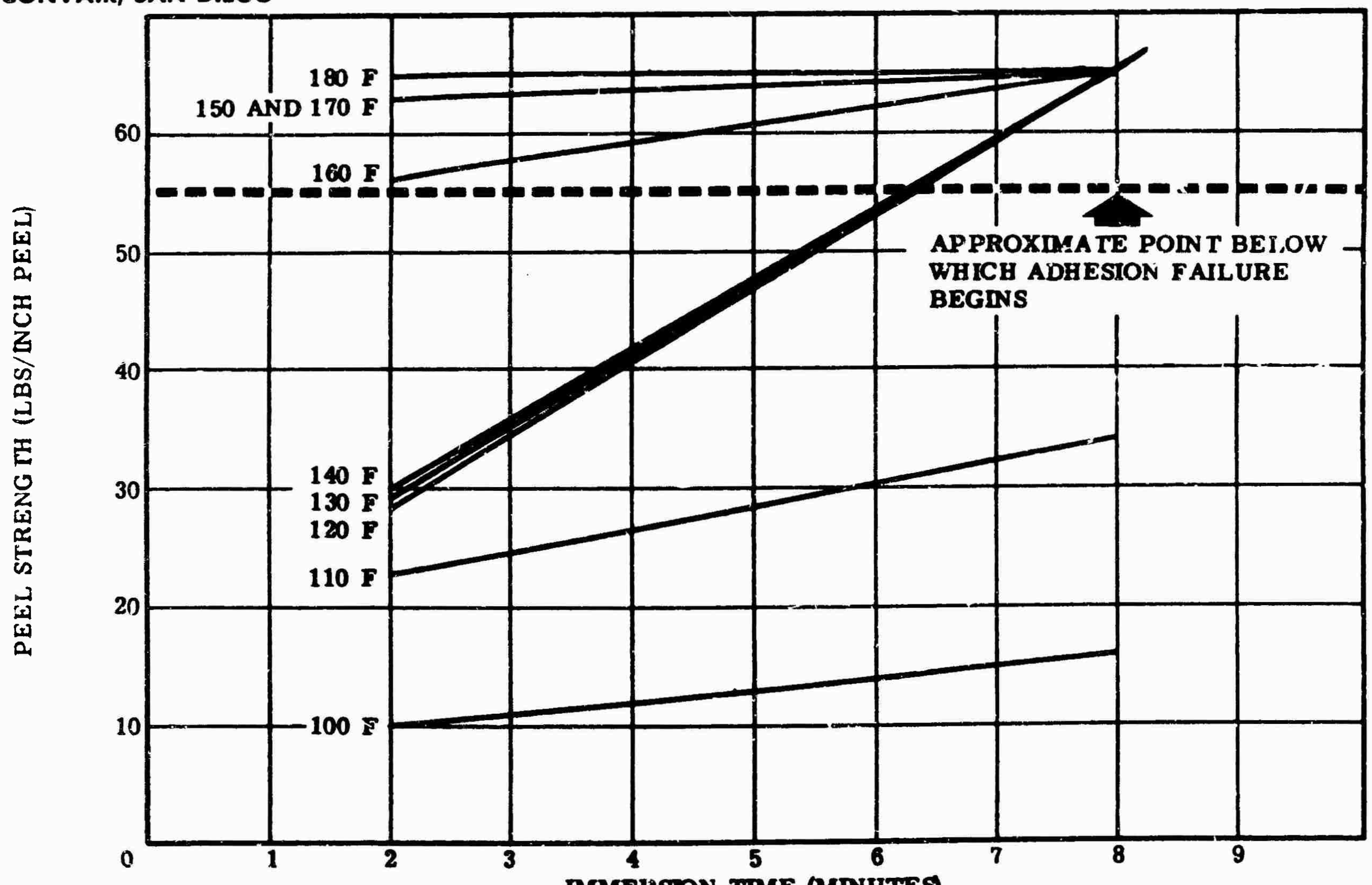


FIGURE 5 - F. P. L. CLEANER-EFFECTS OF TEMPERATURE-TIME VARIABLES ON PEEL STRENGTH OF METLBOND 4021 ADHESIVE - 2024-T3-CLAD ALUMINUM ALLOY

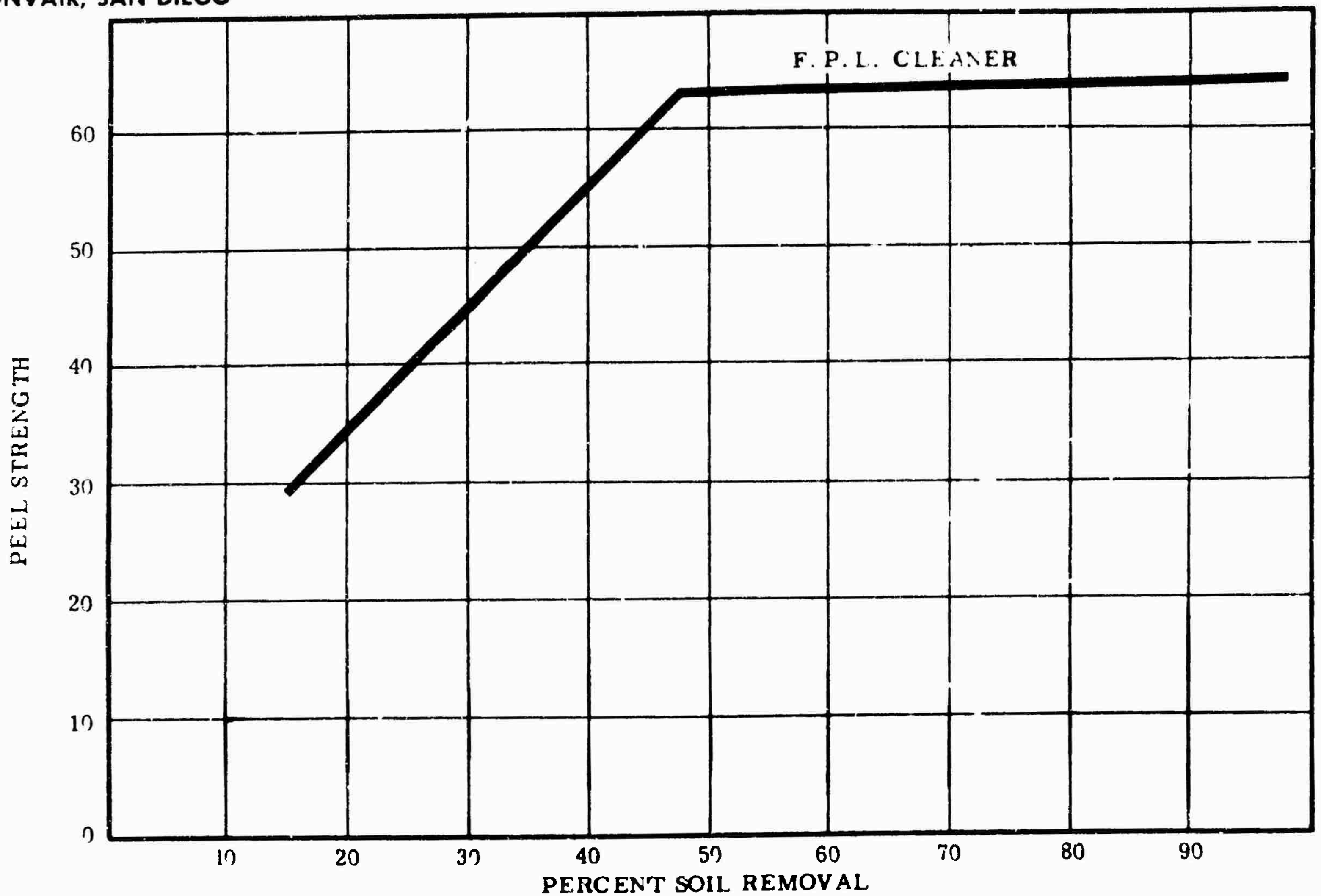


FIGURE 6 - PEEL STRENGTH VS. SOIL REMOVAL FOR F. P. L.

VI. DEVELOPMENT OF THE PROJECT

B. Correlation of Adhesive Bond Strength with Surface Ion Adsorption: (continued)

Ten discs were placed in each of the solutions and the containers placed in a constant temperature bath at 32° C. The discs were removed from the bath singly at selected time intervals. One side of the discs and the rim were sanded to remove the radioactive material and a count was made of the activity present on the remaining disc face. The total number of atoms of chromium present on these surfaces was calculated and plotted as a function of time.

The results of these tests indicated that the amount of chromium adsorbed from a solution at adsorption saturation was proportional to the concentration of the solution in the range considered. ( See Figure 7 )

Adhesive tensile shear and peel tests were run on aluminum treated with sodium dichromate solutions of the concentrations considered in the adsorption studies. The aluminum alloy used to make the specimens was the same as that used earlier.

The specimens were hand wiped with methyl ethyl ketone immersed in boiling concentrated nitric acid for two minutes, removed, rinsed in distilled water and dried at ambient temperatures. They were then placed in solutions of various concentrations of sodium dichromate for 120 hours, removed, rinsed, dried, and bonded. Bonding and testing was done in the same manner as in the previous test, with noted exceptions[1].

1. Adhesive testing in the chromium adsorption studies was the same as in the

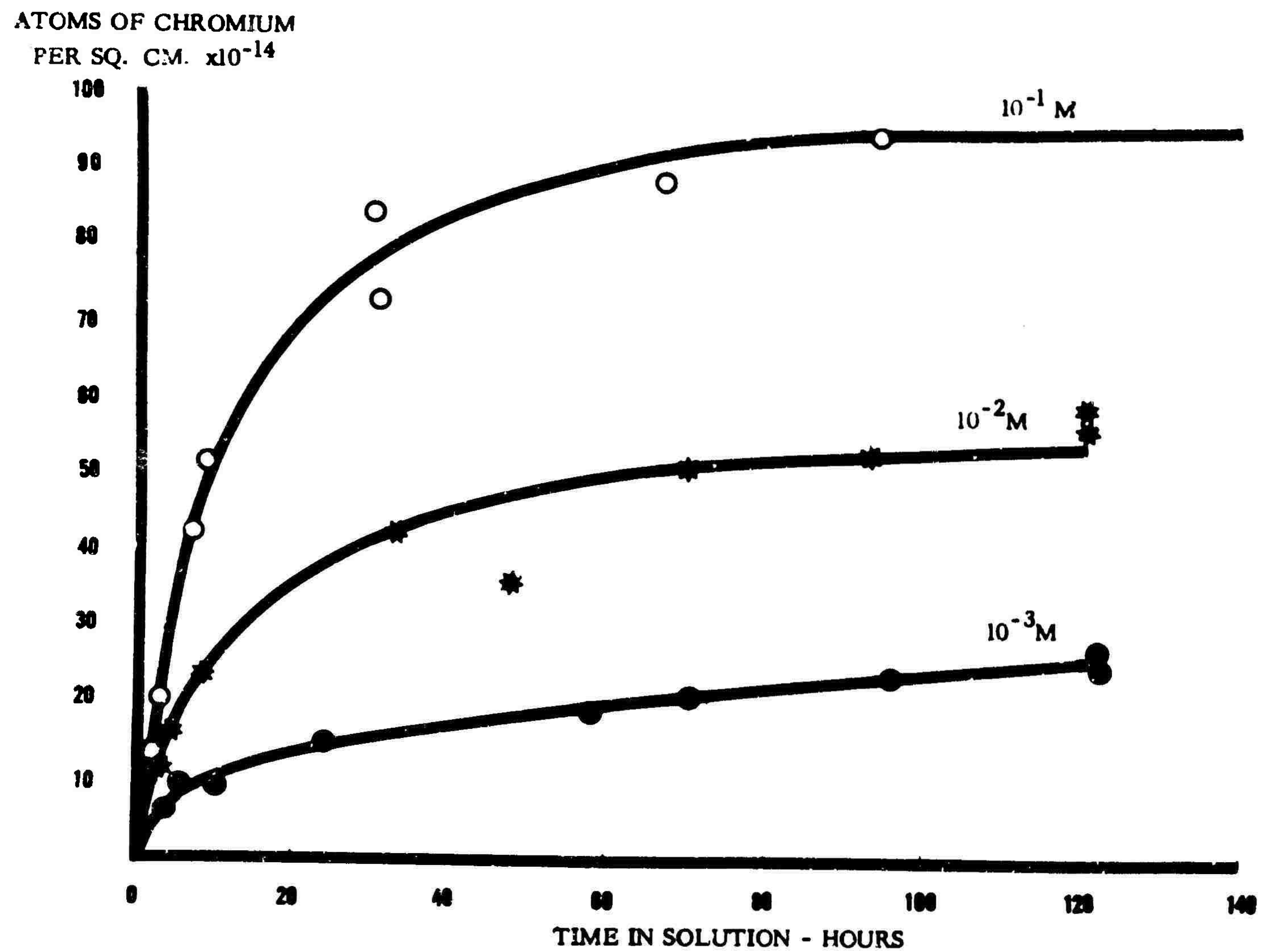


FIGURE 7 ADSORPTION ISOTHERMS; Chromium Adsorbed on Aluminum Surfaces from Dichromate Surface Solutions (32° C.)

VI. DEVELOPMENT OF THE PROJECT

B. Correlation of Adhesive Bond Strength with Surface Ion Adsorption: (continued)

1. (cont'd.)

previous study of cleaning efficiency, except that specimens were not cleaned in the commercial cleaners, but rather as described. EC 1660 primer was used in these tests and the bonding tape was AF-32. EC 1660 and AF-32 are products of Minnesota Mining and Manufacturing Company.

Failures in the tensile shear test specimens occurred usually at the metal to prime interface. Among the peel specimens, those having no chromium on the surface failed at the metal to prime interface; those having the greatest amount of chromium on the surface exhibited predominantly a cohesive type of failure, while intermediate specimens showed mixed types of failure. (See Fig. 8 and Tables IV and V.)

VII. ACKNOWLEDGEMENTS

Acknowledgement is made to H. R. Barringer and B. H. Faulkenberry, both formerly of the Materials and Processes Laboratory, Convair-San Diego, who performed work for the initial phase of the experimental work on this project. Acknowledgement is also extended to Anita Mc Gowan, co-worker on this project.

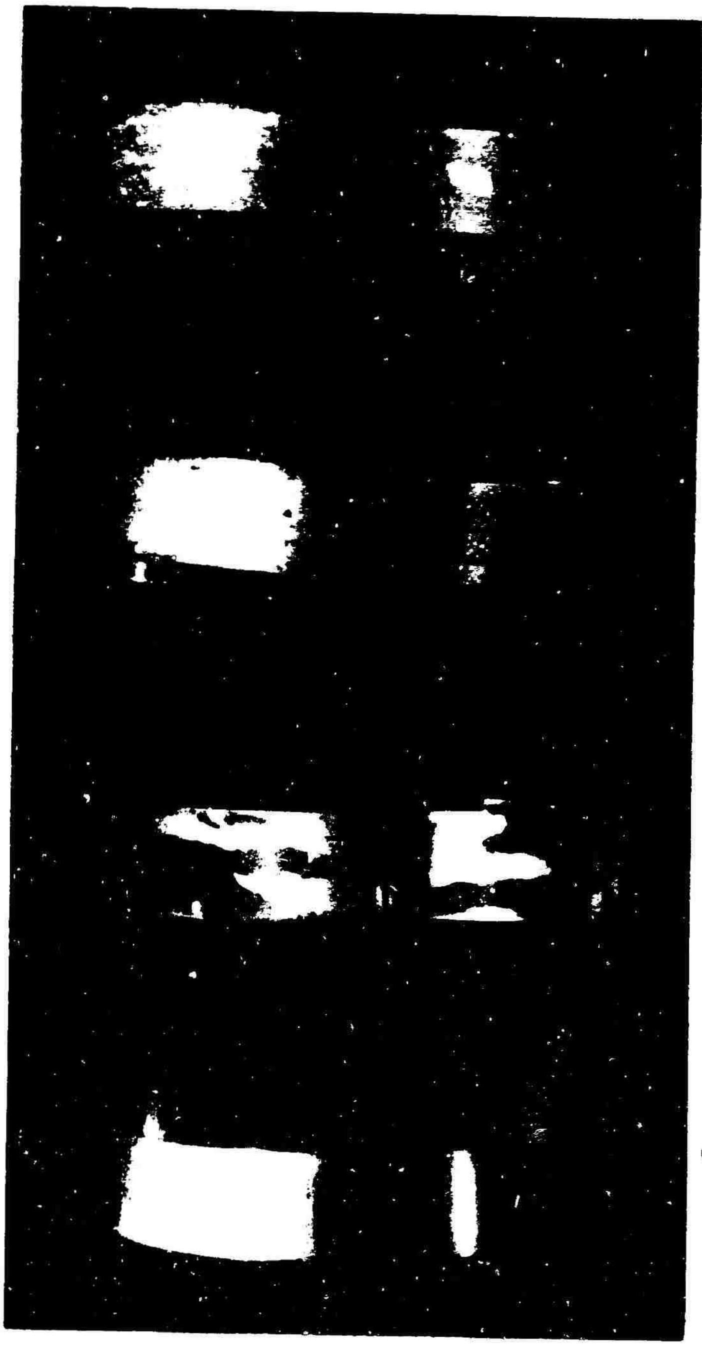


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Figure 8 EFFECT OF Cr, ADSORBED ON SURFACE, ON ADHESIVE PEEL TEST SPECIMENS

TABLE IV

PEEL STRENGTH OF AF-32 ADHESIVE ON 2024-T3 CLAD ALUMINUM ALLOY HAVING VARIOUS AMOUNTS OF CHROMIUM ABSORBED ON THE SURFACE

(TESTS PERFORMED AT ROOM TEMPERATURE)

| SPECIMEN DESIGNATION | CONCENTRATION OF CHROMIUM SOLUTION USED TO TREAT SPECIMENS | NUMBER OF SPECIMENS | AVERAGE PEEL STRENGTH LBS/INCH WIDTH | STANDARD DEVIATION |
|---|---|---|---|---|
| A | 0 | 8 | 21.6 | 3.5 |
| B | $10^{-3}$ M | 8 | 33.1 | 7.0 |
| C | $10^{-2}$ M | 8 | 41.9 | 7.1 |
| D | $10^{-1}$ M | 12 | 54.2 | 5.2 |

TABLE V

TENSILE SHEAR STRENGTH OF AF-32 ADHESIVE ON 2024-T3 CLAD ALUMINUM ALLOY HAVING VARIOUS AMOUNTS OF CHROMIUM ABSORBED ON THE SURFACE

( TESTS PERFORMED AT -67° F)

| SPECIMEN DESIGNATION | CONCENTRATION OF CHROMIUM SOLUTION USED TO TREAT SPECIMENS | NUMBER OF SPECIMENS | AVERAGE TENSILE SHEAR STRENGTH (PSI) | STANDARD DEVIATION |
|---|---|---|---|---|
| A | 0 | 8 | 3394 | 176 |
| B | $10^{-3}$ M | 8 | 4640 | 254 |
| C | $10^{-2}$ M | 8 | 4892 | 506 |

## BIBLIOGRAPHY


1. Barringer, H. R. and Gunthorp, S.; Investigation of Aluminum Alloy Surface Treatments for Adhesive Bonding; Model MRS 55-146; Convair San Diego Report No. 9727, 1956.

2. Barringer, H. R. and Picotte, G. L.; Investigation of Sulfuric Acid Sodium Dichromate Aluminum Alloy Cleaners for Adhesive Bonding Model MRS 56-146; Convair-San Diego Report No. 56-250, 1957.

3. Malley, N.; Metal Cleanliness Tester; Convair-San Diego Report Manufacturing Development and Process Spec. 1957.

4. Mappus, L. A., Bergstrom, B. and Malley, N.; Effects of Natural Aging of Metlbond 4021 Tape; Model F-106, Report 56-871, Convair-San Diego, 1958.

5. Lindsay, R. Jr.; Treatment of Metal Surface for Adhesive Bonding; Franklin Inst. Lab. R. D., WADC Tech. Report 55-87, Part VI.

6. Bickford, H. G. (Editor); Treatment of Metal Surface for Adhesive Bonding; Franklin Inst. Lab. R. D., WADC 55-87, Part IV, 1958, AD 150993.
   Drew, James B.; Theory of Bonding; Part VIII, p 18.

7. Kafalas, J. A. and Gatos, H. C.; Apparatus for the Direct Measurement of Adsorbtion on Solid Surfaces from Liquids; The Review of Sc. Inst., 29 (1), 1958.

8. Hackerman, N. and Powers, R. A.; Surface Reaction of Chromium in Dilute $Cr^{51}0^{4}$ = Solutions; Journal of Physical Chem. 57, pp 139 - 142, February, 1953.

9. Brown, R. M.; A Study of Aluminum Surface Properties with Tagged Organic Molecules; Douglas Aircraft Co. Santa Monica, 21 October, 1959.